

Introduction

Bromine is one of the halogen elements belonging to group 17 of the periodic table, which also includes F, Cl and I. The element has an atomic number of 35, an atomic mass of 80, four main oxidation states (-1, +1, +3 and +5), of which the -1 state is most common in nature, and two naturally occurring isotopes (^{79}Br and ^{81}Br) with abundances of 50.54% and 49.46% respectively.

Bromine is a lithophile (atmophile) element, generally associated with volatile components, and is highly concentrated in the upper mantle and crust of the Earth (Kaufmann 1999a). Its occurrence in rock-forming minerals is most commonly associated with substitution of Cl^- ions for Br^- ions in chlorine-rich minerals such as sodalite and eudialyte. Both ions have similar ionic radii (Cl^- 181 pm; Br^- 196 pm) allowing Br^- to occupy Cl^- ion sites within the mineral lattice (Kogarko and Gulyayeva 1965). Bromine minerals are very rare, with only three polymorph silver halides being recorded: bromyrite or bromargyrite AgBr , embolite $\text{Ag}(\text{Cl},\text{Br})$ and iodobromite $\text{Ag}(\text{Cl},\text{Br},\text{I})$ (Hey 1950). The geochemistry of Br is closely related to water chemistry and to evaporite deposits (Kabata-Pendias 2001).

Chlorine-rich minerals such as sodalite and eudialyte contain $\geq 34 \text{ mg kg}^{-1}$ Br. The average abundance of Br in the Earth's crust is 2.5 mg kg^{-1} (Taylor 1964). In igneous rock types, Br concentrations rarely exceed 4 mg kg^{-1} ; glassy volcanic rocks retain more Br than their crystalline counterparts, and there is a strong correlation between Cl and Br contents in volcanic rocks (Sugiura 1968). Sedimentary rocks contain relatively high concentrations of Br, commonly associated with detrital organic material (Cosgrove 1970). Sediments formed under saline conditions have been found to contain higher concentrations of Br when compared to those from fresh water settings. Bromine concentrations within sediments tend to decrease with depth of burial, and the associated pore water often contains more Br than the sediments themselves (Wedepohl 1978). Coal and organic matter accumulate Br, and a strong correlation of Br with organic carbon has been

reported for both superficial sediments and soil (Kabata-Pendias 2001).

Bromine enrichment in top soil horizons is principally an effect of its precipitation with rain (Kabata-Pendias 2001). Despite the observed sorption capacity of Br by Al and Fe hydroxides, organic matter and clays, it is easily leached from soil profiles and transported to marine basins in large amounts. Generally, Br has a significant positive correlation with exchangeable calcium and organic carbon, especially in calcareous soil. The Br content in soil varies from 5 to 40 mg kg^{-1} (Kabata-Pendias 2001).

Bromine forms highly soluble salts with both alkali and alkaline earth metals. In natural water it is always present as the bromide ion, Br^- . It is the eighth most abundant solute in sea water, with an average concentration of 67 mg l^{-1} (Hem 1992). Natural brines and thermal waters also have high bromide concentrations, e.g., some Japanese thermal water contains up to 60 mg l^{-1} Br^- (Kikkawa and Shiga 1966). Sources include desorption from clay surfaces and breakdown of organic material (Hitchon *et al.* 1971). In coastal areas, higher bromide concentrations in groundwater can be attributed to infiltration of sea water. Bromide concentrations in rainwater and snow are very variable, ranging from 5 to $150 \text{ } \mu\text{g l}^{-1}$ (Fuge 1973). The average abundance of Br^- in river water is quoted as $20 \text{ } \mu\text{g l}^{-1}$ by Turekian (1969). River water concentrations of bromide are controlled in part by precipitation, the chemistry of tributaries and drainage basin geology, the last having the most influence.

The Cl:Br ratio is an important factor for defining different geological environments, and is dependent on the hierarchy of salt precipitation from evaporation of ocean water; it is assumed that the modern average Cl:Br ratio of approximately 300:1 has not changed significantly with time (Kaufmann 1999a):

- Cl/Br = 300, oil fluid, brine or formation water derived directly from ocean water;
- Cl/Br >300, oil fluid, brine or formation water derived from halite salt, and
- Cl/Br <300, oil fluid, brine or formation water derived from residual solutions

produced by partial precipitation of halogen salts.

Bromine was traditionally used to produce ethylene dibromide, a lead scavenger used in the production of antiknock compounds in petrol. However, this source has been drastically reduced because of concerns over the amount of Pb in the environment. Bromine is also used in the manufacture of fumigants (methyl bromide) for agricultural purposes, flame proofing agents, water purification compounds and dyes, as well as the production of photographic chemicals; it is also a component of K-fertilisers (Kabata-Pendias 2001).

Bromine has not been classified as being essential to human health although, in the form of

KBr or NaBr, has anti-seizure properties and is effective in the treatment of hyperthyroid conditions. Because of its high reactivity with other elements, inorganic bromides found in the environment pose no toxicological risk. However, bromine in liquid state, or even more so as vapour, is toxic, causing severe irritation and burning of the eyes, respiratory organs, skin and the gastro-intestinal tract. Bromides do not damage plants and are not necessarily essential. Many marine plants, particularly kelp, are a rich source of bromine and iodine.

Table 14 compares the median concentrations of Br in the FOREGS samples and in some reference datasets.

Table 14. Median concentrations of Br in the FOREGS samples and in some reference data sets.

Bromine (Br)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median mg kg⁻¹
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	1.6
Water (Br)	FOREGS	808	Filtered <0.45 µm		<0.01 (mg l⁻¹)
Water ²⁾	World	n.a.	n.a.		0.02 (mg l ⁻¹)

¹⁾Rudnick & Gao 2004, ²⁾Ivanov 1996.

Br in stream water

Bromide values in stream water range over two orders of magnitude, from 0.03 to 2.97 mg l⁻¹ (excluding an outlier of 7.90 mg l⁻¹), with a median value below the analytical detection limit of 0.03 mg l⁻¹.

The lowest Br concentrations of 0.04 mg l⁻¹ in stream water constitute close to 75 percent of all determinations. This poor analytical performance makes a reliable discussion of the Br distribution impossible. The low values are found throughout most of Europe, covering all terrains, from Precambrian to Alpine Orogen.

Enhanced bromide concentrations in stream water occur in southern Portugal over sediments of marine origin, where slow-flowing groundwater with long residence time picks up a high proportion of easily dissolved ions, and climatic conditions favour evapotranspiration, increasing salts in solution. An isolated anomalous value in north-central Spain, in the Ebro basin, can be ascribed to evaporitic lithologies with marl, clay and gypsum. Two anomalous samples in central Spain occur in streams draining evaporitic halite-bearing

sediments (upstream) of the Triassic Keuper facies; the same setting in southern Spain, but here the Triassic evaporites were tectonically reworked and resedimented during the Alpine orogeny (olistostromic complexes in the Sub-Betics). High Br values also occur in Brittany, central and southern England (associated with agricultural processes), on the northern coast of the Netherlands and western Denmark on Quaternary deposits (possibly related to saltwater intrusion, *i.e.*, saline coastal aquifers discharging groundwater into streams). High concentrations of bromide occur throughout central, south-eastern, and insular (Sicily and Sardinia) Italy on Alpine Orogen terrains and are associated with occurrences of alkalic volcanics and evaporites. Enhanced values in the Pannonian basin of Hungary may be related to hydrothermalism. Grouped and isolated high values may also be related to areas of intense agricultural activity.

The bromine distribution pattern follows that of elements typical for sea spray and evaporates: Na, Cl, and I. In Italy, there is a possible volcanic origin of Br.